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Symposium K, "Materials Synthesis by Thermal Spraying"
held at the 1999 MRS Fall Meeting
Boston MA during November 29-December 3, 1999

Final Technical Report

Call for Papers

Symposium K will focus on materials synthesis by thermal spraying. The need for engineered coatings with controlled composition and microstructure is increasing because of increasing demands on the materials properties in a variety of applications such as aerospace, environment, catalysis, and electrodes. A possible gain in productivity by using thermal spraying as a process for materials synthesis is a strong driving force that is coming from the industry. This symposium is intended to provide current knowledge in the field of thermal spraying synthesis of materials including ultrafine powder synthesis, with highlights on processing, modeling and diagnostics and nanostructure materials applications and characterization. As part of the symposium, an honorary session will be devoted to Professor Herbert Herman from SUNY-Stony Brook for his overall contribution in the field of thermal spraying. This symposium seeks to bring together researchers from academia and industry to discuss fundamental mechanisms and phenomena, as well as processing in the materials synthesis and thermal spraying field.

Topics of interest include:

- Materials synthesis by thermal spraying
- Diagnostics applied to thermal spraying and materials synthesis
- Modeling of processes, nucleation, growth, crystal growth, non-equilibrium thermodynamics
- Ultrafine powders
- Nanostructures
- Application of new thermal spraying processes in materials synthesis
- Applications and characterization of nanostructures
- Technologies such as thermal plasma, combustion spray, and arc spray

Symposium Highlights

Symposium K featured an Honorary Symposium for Herbert Herman, director of the Center for Thermal-Spray Research, an NSF Materials Research Science Engineering Center at SUNY-Stony Brook, for 15 years as Editor-in-Chief of *Materials Science and Engineering*, and Leading Professor of the Department of Materials Science and Engineering in the area of spray-coating formation and evaluation. In his opening remarks, P. Fauchais (Universite' de Limoges, France) particularly noted Herman's pioneering role in bringing science into thermal-spray coatings through his work on process control, feedstock-material chemistries, particle characteristics, coating characterization according to the process, and standardization.

Highlights of this symposium included C.C. Berndt's (SUNY-Stony Brook) report that coatings made by spraying nanoppowders of partially stabilized zirconia (PSZ) and alumina (Al_2O_3) exhibit improved mechanical and thermal properties, and that the PSZ coatings contain only the nontransformable tetragonal phase of zirconia (ZrO_2). Cold spraying, so the nanostructured phase is not melted, apparently is the "secret." R.A. Neiser (SNL) discussed the cold-spray process for depositing metal and composite powders at close to room temperature. It was found that at low velocities (~250 m/s), the particles tended to bounce off the substrate surface, but as the velocity was increased to ~900 m/s, they stuck, and very high deposition efficiencies could be obtained. There exists a minimum velocity, the critical velocity (V_{crit}) for deposition that can be used, along with the spread of the particle velocities around the mean, to calculate the deposition curve. At SNL, the factors influencing V_{crit} for metal-metal deposition are being investigated. One finding is that the oxygen content of cold-sprayed Cu is essentially the same as the initial powder (0.3 wt.%), and the thermal conductivity of the coating (317 W/m K) is very high compared with conventionally sprayed Cu. Another is that the hardness of the powder has the largest influence on V_{crit} (need to increase velocity with increasing hardness), but the hardness of the substrate has no effect.

F. Jansen (Sulzer Innotec, Ltd.) described the thermal-shock resistance, thermal-insulation efficiency, and corrosion resistance of thermally sprayed dicalcium silicate (Ca_2SiO_4) coatings as comparable to yttria-stabilized zirconia coatings, and promising as thermal-barrier coatings up to 900°C. A. Dent (SUNY-Stony Brook) reported the potential of high-velocity oxygen-flame-sprayed barium titanate (BaTiO3), alumina (Al_2O_3), and magnesium aluminate ($MgAl_2O_4$) as dielectric layers with functional properties for electronic components. A number of materials-characterization techniques (SEM, TEM, XRD) were used to investigate phase transformations occurring within these materials as a consequence of thermal spraying. The advantages of thermal spray are that it is a quick and easy way to coat large areas, and it is a high-throughput technology.

S. Sampath (SUNY-Stony Brook) closed the symposium by noting that Herman's legacy was to develop an integrated approach to thermal spray, to establish some fundamental relationships at each stage with the objective of developing correlations between the intrinsic physics and the processing conditions. The goal is optimizing the process to produce the desired microstructures for the coating design and performance.

Attachment – F99K Abstracts

SYMPOSIUM K

Thermal Spray–Materials Synthesis by Thermal Spraying

November 29 – 30, 1999

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* Invited paper

SESSION K1: SPRAY PROCESS CHARACTERIZATION BY MODELING AND DIAGNOSTICS
Chairs: Christian Moreau and Emil Pfender
Monday Morning, November 29, 1999
Room 309 (H)

8:30 AM *K1.1
OXIDATION OF IRON PARTICLES IN Ar-H_2 D.C. PLASMA JETS FLOWING IN AIR AND OF THE RESULTING COATINGS. Pierre Fauchais, J.F. Coudert, Armelle Vardelle, Université de Limoges, Laboratoire Science des Procédés Céramiques et de Traitements de Surface, Limoges, FRANCE.

Atmospheric plasma spraying (APS) results in oxidized metal and alloy coatings thus reducing their thermal and mechanical properties compared to those sprayed in a controlled atmosphere. To limit this oxidation, the way it occurs has to be better understood. This can be achieved by: 1) Modeling the jet flow and air entrainment using a k-e model with low Reynolds to account for the laminar core of the jet. However, such a model does not account for the 'piston flow' of the jet induced by the arc root fluctuations especially those due to the restrike mode; 2) Modeling the metal particle reaction with the oxygen during its flight within the plasma jet taking into account both diffusion and convection within the particle; 3) Measuring the entrained oxygen in the plasma jet core by emission spectroscopy and the plasma plume by an enthalpy probe coupled with a mass spectrometer and comparing the results with those of the k-e model; 4) Collecting particles in flight at different distances from the torch nozzle exit and quenching them in order to analyze them by SEM and XRD; 5) Studying the possible protection of the particles by an alumina shell; 6) Studying the effect of the particle oxygen content on its wettability; 7) Studying the effect of the substrate preheating temperature on substrate oxidation and coating adhesion/cohesion and oxidation. All these points will be illustrated for an Ar-H_2 d.c. plasma jet, spraying low carbon steel particles covered or not by an alumina shell (using mechanofusion technology) deposited on steel substrates.

9:00 AM *K1.2
DEFORMATION AND SOLIDIFICATION PROCESS OF A SUPER-COOLED DROPLET IMPACTING TO THE SUBSTRATE UNDER PLASMA SPRAYING CONDITIONS. Toyonobu Yoshida and Yongkee Chae, The University of Tokyo, Dept of Materials Engineering, Tokyo, JAPAN.

To date, many modeling efforts related to the deformation and solidification processes of a droplet impacting on the substrate under plasma spraying conditions have been reported. However, to the authors' knowledge, no modeling effort has dealt with the super-cooling effects on the deformation and solidification processes, though much evidence of super-cooling effects has been reported. In this paper, we will show the first results derived from our recent modeling efforts, which clearly show the strong effects of the super-cooling conditions on the deformation and solidification processes. As expected, for example, we could depict a significant decrease in deformation ratio, D/d, to less than 2.0, and also a faster solidification front velocity of around 1-2 m/s. Although the small deformation ratio is clearly caused by the larger value of viscosity under super-cooled conditions, the rapid solidification is eventually caused by the super-cooling. We applied the modified SOLAVOF 2D code to the calculation, and we could not simulate a dendritic growth, but the model clearly suggest that plasma sprayed particles may be actually in super-cooled state, and any modeling efforts should include the super-cooling effects.

9:30 AM *K1.3
MODELLING OF THE FORMATION OF THERMAL SPRAY COATINGS. J. Mostaghimi, M. Pasandideh-Fard, R.G. Azar, S. Chandra, University of Toronto, Department of Mechanical and Industrial Engineering, Toronto, Ontario, CANADA.

Thermal spray coating processes are concerned with the manufacturing of functional coatings by heating, melting, and accelerating powdered materials in a high temperature, high velocity gas stream, and depositing them onto a surface. Because of the nature of the process, thermal spray coatings have porosity. Understanding how porosity is formed and how it relates to the particle impact conditions is of great fundamental and practical interest. In this presentation, we report the results of a model, which is developed to predict the formation of thermal spray coatings. Of great importance to this model, is our ability to simulate the impact and solidification of a molten droplet on an arbitrary shape surface. For this purpose, we have developed a three-dimensional model of droplet impact and solidification [1,2]. To simulate the formation of coatings, realistic particle impact conditions, e.g., velocity, size, and position of the impact on the substrate, are randomly selected from given distribution functions. Based on these selections, splat shapes are predicted using the model described in references [1,2] and formation of the coating is predicted splat by splat. The result of these simulations will provide insight into the dynamics of the coating formation and, possibly, how porosity relates to the operating conditions. References [1] M. Bussmann, J. Mostaghimi, and S. Chandra, On a Three-dimensional Volume Tracking Model of Droplet Impact, Phys. Fluids, 11, pp.1406-1417, 1999. [2] M. Pasandideh-Fard, J. Mostaghimi, and S. Chandra, 3D Model of Droplet Impact and Solidification: Impact on a Solidified Splat, Proc. Int. Symp. Plasma Chemistry (ISPC-14), Prague, Czech Republic, Aug. 2-6, 1999.

10:30 AM K1.4
MODELING OF PHASE SELECTION AND MICROSTRUCTURE FORMATION OF SINGLE SPLATS IN PLASMA-SPRAYED COATINGS. Guo-Xiang Wang, Department of Mechanical Engineering, The University of Akron, Akron, OH.

Plasma-sprayed coatings are made of small splats formed when molten particles impact at a high speed on a substrate. The quality and the properties of a coating therefore strongly depend on the phases and microstructures of each splat. This presentation will discuss our recent efforts in modeling of phase selection and microstructure development of single splats in plasma-sprayed coatings. Emphasis is on treatment of nucleation kinetics of both stable and metastable crystalline phases, non-equilibrium growth kinetics, and solidification dynamics, and on the integration of solidification kinetics and heat and mass transport. Examples will be given to demonstrate applications of the model to coatings of both metallic and ceramic materials. It will be shown that, by using the classical nucleation theory, the model can successfully predict the selection of metastable phases in an alumina system, and calculate the grain density and size distribution that compare reasonably well with experimental measurements. The model can also be used to explain the variation of the size of the grains in Mo splats sprayed on different substrates (glass and metallic), and formation of nano-size particles in a partially yttria-stabilized zirconia coating sprayed on a low-temperature substrate.

10:45 AM K1.5
CORRELATION BETWEEN VELOCITY AND TEMPERATURE OF THERMALLY SPRAYED PARTICLES. Yuepeng Wan, Qiang Deng, Hui Zhang, Sanjay Sampath, Vish Prasad, Center for Thermal Spray Research, SUNY Stony Brook, NY; James Fincke, Idaho National Engineering and Environment Lab, ID.

In thermal spray process, the velocity and temperature of impacting particles are controlled by many parameters, such as the operating conditions of plasma or combustion torch, the particle injection conditions, and the powder material characteristics. One issue that arises is: can the particle velocity be changed independent of temperature? The answer to this question requires understanding of the relationship between temperature and velocity of thermally sprayed particles. This paper analyzes this intrinsic relationship by deducing and solving a set of integrated equations for particle velocity and temperature. Based on the classic theory for the flow field of free turbulent jets, the momentum and energy equations for individual particles are simplified according to the spray conditions considered. Analytical correlation or ordinary differential equations are consequently obtained for the velocity and temperature of particles with different sizes. The results of the simple correlation reveals the basic relationship between particle temperature and velocity. The analytical or semi-analytical solutions are compared with experimental results and multi-dimensional numerical simulation results performed under the similar spray conditions. Results show that the velocity and temperature of particles are highly correlated, as already exhibited by some experimental investigations. Possible approaches for the effective control of particle velocity and temperature are discussed in the present study.This research was supported by NSF through the MRSEC Program under Award No. DMR-9632570.

11:00 AM K1.6
OBSERVATION OF ARC INSTABILITIES IN A PLASMA SPRAY TORCH. Zheng Duan, Joachim Heberlein, University of Minnesota, Department of Mechanical Engineering, Minneapolis, MN.

Arc instabilities during plasma spraying can strongly influence the quality of the coating. In an effort to enhance our understanding of the instabilities, we have investigated the arc anode attachment movement in a plasma spray torch using end-on observation of the arc with a high speed camcorder with framing rates as high as 45,000 frames per second. The recording of the images has been synchronized with oscilloscope traces of the voltage. The torch has been operated with various anode conditions, at different current levels, and with different gas flow rates and gas injection methods. This allowed observation of the previously identified different instability modes, i.e. the restrike, takeover and steady modes. The observations show that the arc has a clearly visible, constricted anode attachment in the

restrike mode, a broad and diffuse attachment in the takeover mode, and no clearly identifiable attachment in the steady mode. In the restrike mode, the anode attachment has been found to continuously move around the circumference of the anode nozzle for swirl injection of the plasma gas. While the thickness of the cold gas boundary layer, which is clearly visible between the bright arc and the anode surface, is believed to be the primary factor in determining the instability mode, the turbulence level and the anode jet can also have strong influences on the arc dynamics. The turbulence mainly results in continuous small oscillations of the arc column, and the anode jet may lead to rapid jumps of the anode attachment to another location. Observation of the corresponding plasma jet images shows a strong influence of the arc instabilities on the jet length and the jet stability, and the turbulent entrainment of the cold gas. All these factors affect the heating and acceleration of the spray particles and, consequently, the coating quality.

11:15 AM K1.7
FLUID DYNAMIC CALCULATIONS OF THE HIGH VELOCITY OXYGEN FUEL (HVOF) THERMAL SPRAY PROCESS. Q. Xu[1], G. Trapaga[2] and E.J. Lavernia[1]; [1]Dept. of Chemical and Biochemical Engineering and Materials Science, Univ. of California, Irvine, CA; [2]Dept. of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Computational fluid dynamic methods are implemented to simulate internal and external flows in a high velocity oxygen-fuel (HVOF) thermal spray torch as well as their interactions with injected powders. A one-step global reaction model, which takes into account dissociation at high temperatures, is used to represent the combustion process of oxygen and fuel. The calculated results show that the mixture of inlet gases and chemical reaction products is accelerated within the converging part of the nozzle to reach sonic condition at the nozzle throat, and is further accelerated to develop a supersonic flow within the diverging section of the nozzle as temperature and pressure decrease. When the supersonic jet exits into the ambient air, it matches the atmospheric pressure through a series of expansion and compression waves, which are captured by the calculations. Subsequently, the supersonic jet decelerates, spreads, cools down, and becomes a subsonic flow as a result of mixing with the surrounding air. Heat and momentum transfer to the particles take place primarily in the diverging part and the supersonic core of the external jet. The velocities and temperatures of individual particles are strongly related to their sizes and specific operating conditions. These preliminary results provide some insight into the behavior of this system and represent the first step in addressing the microstructural evolution of coatings produced by the HVOF thermal spray process.

11:30 AM K1.8
MODELING OF HIGH POWER PLASMA SPRAYING. Vladimir Belashchenko, Victor Sedov, Andrei Ivanov, Tetyana Shmyreva, TAFA Inc., Concord, NH.

Thermal conditions of coating formation are considered for 100 kW and 200 kW plasma guns. Results of the modeling are compared with results of experimental evaluation of several ceramic coatings.

11:45 AM K1.9
THE MODEL OF CONSECUTIVE NON-EQUILIBRIUM SOLIDIFICATION OF MELT DROPLET AT PLASMA SPRAYING. Ruslan Abdulkhalikov, Alexander Fedorchenko, Inst of Thermophysics SB RAS, Novosibirsk, RUSSIA.

In the works of Madejski[1], Fedorchenko & Solonenko[2], analitycal solutions to the problem of solidification of the melt drop during its collision with the base were obtained on the basis of the equilibrium crystallization model. The results of experimental investigations on the crystallization of small metallic droplets (Turnbull & Cech[3]) show that the supercooling of metallic drops (having the diameter of 20-400 μm) can reach several hundreds of degrees. In order to take into account the physical peculiarities of the solidification process in these conditions, it is necessary to use the crystallization kinetics itself. Simple estimates show that the interaction regimes "droplet-surface" for which the testing of the results in the theoretical works mentioned above was made, refer just to this case (cooling rates of the order 10^6 - 10^8 K/s, and supercooling is of the order 200-400K). Use of the theory of equilibrium crystallization in the range of the parameters listed is not justified. Therefore, the purpose of the given paper is to developed the physical and mathematical model of solidification of the limited volumes of metal melts in the conditions of ultrarapid quenching and obtain, on its basis, the criteria of equilibrium and non-equilibrium solidification. References: [1] Madejski, J. Solidification droplets on a cold surface, Int. J. Heat and Mass Transfer,1976, V.19, N.9. [2] Fedorchenko, A.I. & Solonenko, O.P. Dynamics of crystallization processes of molten particles at their interaction with surface."Plasma Jet in the Development of New Materials Technology", VSP, The Netherlands,1990. [3] Turnbull, D & Cech, R.E. Microscopic observation of the solidification of small metal droplets, J. Appl. Phys., 1950, V.21, N.8.

SESSION K2: HONORARY SESSION FOR PROFESSOR HERMAN ON SPRAY COATING FORMATION AND EVALUATION

Chairs: Mitchell R. Dorfman and Richard A. Neiser
Monday Afternoon, November 29, 1999
Room 309 (H)

1:30 PM OPENING REMARKS by Prof. Fauchais

1:45 PM *K2.1
THERMAL SPRAYING AS A MEANS TO ACHIEVE NANOSCALE STRUCTURES. Christopher C. Berndt, SUNY at Stony Brook, Dept Materials Science and Engineering, Stony Brook, NY.

Thermal spray deposits have the natural, intrinsic ability to form very fine microstructures since they are deposited under rapid solidification conditions that impede grain growth. However, the ability to create nanostructures in a reliable fashion is still elusive to many researchers since it is difficult to control such dynamic manufacturing processes. This presentation will review the methods that have been employed to create nanoscale microstructures. The focus will be on a rationale for the various technologies employed, the feedstock requirements, any special processing protocols, and the coating characteristics that have been measured. The upshot of this world wide activity is that a new generation of thermal spray coatings and technologies are being developed that have superior properties to that of conventionally-produced deposits. These coatings are expect to transition into production plants within the next few years. Acknowledgements: ONR N00014-97-0843, NSF-CTS 9312896, NSF-MRSEC-DMR 9632570.

2:15 PM K2.2
CHARACTERIZATION OF THE COMPLEX, ANISOTROPIC MICROSTRUCTURES OF THERMALLY-SPRAYED CERAMIC DEPOSITS USING SMALL-ANGLE SCATTERING TECHNIQUES - PAST, PRESENT AND FUTURE. Jan Ilavsky [1,2], Andrew J. Allen[1], Gabrielle G. Long[1], Hacene Boukari[1,2], Christopher C. Berndt[3], Herbert Herman[3]. [1]MSEL, NIST, Gaithersburg, MD, [2]University of Maryland, College Park, MD, [3] CTSR, State University of New York, Stony Brook, NY.

Increasing demands on the functional properties and reliability of thermally-sprayed deposits require that we gain better understanding and control of the microstructure of such deposits. New small-angle neutron scattering (SANS) methods have been used over the past several years to characterize the complex microstructure of these deposits and have yielded significant results. The main microstructural features are voids of different type: interlamellar pores, intralamellar cracks and nearly-globular pores. SANS measurements, in combination with results from other techniques, are able to characterize independently each void system. The interlamellar pores and intralamellar cracks have been described in terms of their surface areas. In addition, making use of model assumptions, all three void systems have been characterized separately in terms of their volumes and in terms of their average sizes. The results agree within experimental error with results from other techniques. The progress over the past several years is reviewed and an overview of the results is given. The relationship to other microstructure characterization techniques, and the manner in which they are complementary is also presented. Finally, the most recent results obtained by means of near-surface SANS and its potential for the future are presented.

2:30 PM K2.3
MODELING THE CRITICAL VELOCITY FOR DEPOSITION IN THE COLD SPRAY PROCESS. Delwyn L. Gilmore, Richard A. Neiser, Ronald C. Dykhuizen, Sandia National Laboratories, Albuquerque, NM.

The cold spray process, characterized by near-room-temperature, high-velocity deposition of metal or composite powders, has been the subject of increasing study in the past few years. It has been shown that there is a minimum critical particle velocity for bonding to occur with the substrate. This critical velocity depends on both the particle and substrate materials. However, a fundamental empirical or theoretical model which would link the critical velocity to the intrinsic thermal and mechanical properties of the particle and substrate has not been created. In the current work, experiments were conducted with aluminum powders and substrates. The various alloys were chosen such that the effects of such properties as yield strength, hardness, and ductility might be varied independently of such properties as density, thermal conductivity, and sonic velocity. A model of the critical velocity for deposition can be developed from these experiments and will be presented.

3:15 PM K2.4
PROCESSING EFFECTS ON RESIDUAL STRESSES IN SINGLE PARTICLES DEPOSITED BY PLASMA SPRAYING. Jiri Matejicek, Sanjay Sampath, State University of New York, Center for Thermal Spray Research, Stony Brook, NY.

Changes in processing parameters affect strongly the structure and properties of plasma sprayed coatings and, consequently, their performance. Residual stress in the deposits is a factor that needs consideration, since it has direct influence on the integrity and lifetime of the sprayed component. In order to understand this phenomenon better, a study on the single splat level was undertaken. Residual stresses in isolated molybdenum particles deposited on a stainless steel substrates were studied using x-ray microdiffraction. Two important process parameters were considered: inflight particle energy and substrate temperature. The processing conditions were optimized based on results of a previous process map study, focused on the correlation between plasma torch settings and inflight particle properties. The results will be discussed with respect to the influence of each of these parameters, their relative importance, contribution of quenching and thermal stress component and splat formation. Further, the coating build-up from individual particles and the associated factors influencing residual stress will be discussed.

3:30 PM K2.5
PHASE RELATIONS IN PLASMA SPRAYED CALCIUM SILICATE COATINGS. Franz Jansen, John A. Peters, Sulzer Innotec Ltd., Winterthur, SWITZERLAND; Xiaohan Wei, Mitchell R. Dorfman, Sulzer Metco Inc., Westbury, NY.

Thermally sprayed calcium silicate coating systems may provide cost-effective alternatives to YSZ coatings for selected applications in land-based gas turbines or diesel engines. The advantages of the calcium silicate coatings became particularly evident when a combination of thermal shock resistance and resistance to hot corrosion is required. In this study a range of calcium silicate powder and thermal spray coatings were prepared in order to investigate the influence of both chemical compositions and processing parameters on the phase stability of coatings. The crystal structure of the powders and coatings was determined using X-ray diffractometry while scanning electron microscopy was employed to study the powder morphology and the coating microstructure both before and after thermal cycling. It has been shown that dopants significantly affect the phase stability of coatings at 1200°C.

3:45 PM K2.6
X-RAY COMPUTED MICROTOMOGRAPHY STUDIES OF THERMAL SPRAYED ALUMINA DEPOSITS. Anand Kulkarni, Herbert Herman, State University of New York at Stony Brook, NY; Betsy Dowd and Allen Goland, Brookhaven National Laboratory, NY.

Pores and cracks in thermal sprayed free-standing alumina deposits have been characterized with X-Ray Computed Microtomography (CMT) using the high intensity synchrotron x-ray source at Brookhaven National Laboratory. Cross-sectional maps of linear attenuation coefficients are recorded using a CCD camera with a linear array of detectors. The transmitted values were then processed using a filtered back-projection algorithm to reconstruct the horizontal slices. These slices were then stacked together to build the 3-D microstructural images at a resolution of 2.7 micrometers. Investigations were also performed to produce gray scale images with a bimodal population (grain and void space) which were then computed based upon 3-D medial axis analysis to give information on porosity, specific surface area, pore connectivity and size distribution. The effects on microstructure development were investigated as functions of thermal spray processing (plasma and high-velocity combustion spray) and powder morphology (sol-gel and fused-and-crushed). Thermal, dielectric and mechanical properties of the deposits have been correlated to microstructural features observed.

4:00 PM K2.7
STRUCTURE-DIELECTRIC BEHAVIOR RELATIONSHIPS IN HVOF SPRAYED CERAMICS. Andrew H. Dent, Jonathan Gutleber, Ashish S. Patel, Sanjay Sampath, Herbert Herman, Center for Thermal Spray Research, SUNY, Stony Brook, NY; Ellen Tormey, Sarnoff Corporation, Princeton, NJ.

The HVOF thermal spray process has been used to deposit Al_2O_3, $MgAl_2O_4$ and $BaTiO_3$ powders for potential applications as dielectric layers in electronic packaging. Phase transformations occurring within these ceramics as a result of thermal spraying have been examined using materials characterization techniques including X-Ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The effect of these phase changes as well as the structural inhomogeneities inherent in the HVOF deposit on the dielectric behavior of 25-150μm thick layers of these ceramics has been studied. Layer thickness, uniformity, structural integrity (including porosity) and phase stability have all been shown to play an important role in the ability of these deposits to be used as effective dielectric layers.

4:15 PM K2.8
THERMAL SPRAY: INTEGRATION OF PROCESS, MICRO-STRUCTURE AND PROPERTIES. Sanjay Sampath, Center for Thermal Spray Research Department of Materials Science and Engineering, State University of New York, Stony Brook, NY.

Plasma spraying is a highly dynamic process resulting from rapid heating /accelerating of powder particles in a flame, followed by impact and rapid solidification of the droplets (splats). A splat resulting from the flattening of an individual droplet is the basic building block (unit cell) of the thermal sprayed microstructure. Phase and microstructure of the splats (intrinsic) and the integration of the splats (extrinsic) are both affected by processing condition and the properties of a plasma sprayed deposit are directly related to this complex microstructure. One of the goals of the Center activity is to use an integrated approach to develop fundamental understanding of the deposit formation dynamics as it relates to particle parameters, impact, spreading and solidification. Two parametric variables are addressed for plasma spraying of Molybdenum and zirconia; substrate temperature and particle energy effects. A close coupling of the modeling and experimental activities is undertaken in an effort to synthesize process sensitivities and associated microstructural consequences. They can be represented by the development of process maps which integrates the variables controlling the process and their interactions. Physics based understanding elucidates the underlying mechanisms enhances the confidence in the results. The ultimate objective is manipulation and optimization of the process so as to yield the appropriate microstructures for design and performance. Work suppported by the National Science Foundation, Materials Research Science and Engineering Center program under award no. DMR 9632570

SESSION K3: POSTER SESSION:
Chair: Francois Gitzhofer
Monday Evening, November 29, 1999
8:00 P.M.
Exhibition Hall D (H)

K3.1
PLASMA DEPOSITION OF DIAMOND ON STAINLESS STEEL WITH A NITRIDE OR CARBONITRIDE INTERLAYER. C.F.M. Borges, E. Pfender and J. Heberlein, University of Minnesota, Department of Mechanical Engineering, Minneapolis, MN.

The superlative intrinsic properties of diamond have attracted much industrial interest in developing diamond coating methods. However, it has been well recognized that direct diamond deposition on steel substrates is difficult because of poor adhesion of the diamond to the substrate. The reason for the poor adhesion is that presence of Fe promotes formation of graphite at the interface between the diamond film and the steel substrate. Also, carbon readily diffuses into steel resulting in long nucleation times. We report on a thermal plasma deposition process in which well adhering diamond films have been grown at high rates on stainless steel substrates. The plasma source has been a rf induction plasma torch operating at 20 kW. The substrates have been prepared by plasma nitridation or carbo-nitridation. In an effort to understand the role of the interlayer, the nucleation density has been determined for differently prepared substrates, and the phase changes of the nitride during deposition have been analyzed using X-ray diffraction, scanning electron microscopy, and Raman spectroscopy. The results show that the interlayer consists of iron nitride or carbonitride with a high chromium concentration. These interlayers have been found to act as a diffusion barrier for carbon atoms into the steel. They also appear to reduce the transformation of sp^3 bonds to sp^2 bonds, a transformation which is promoted by the presence of iron and reduced by the presence of chromium. The possibility of producing well adhering diamond layers on steel substrates opens up the potential for new applications of diamond film technology.

K3.2
MULTIMETALLIC OXIDE SINGLE CRYSTAL NANOPARTICLES. T.R. Hinklin and R.M. Laine, Dept. of Materials Science & Engineering, University of Michigan, Ann Arbor, MI.

We recently described methods of producing nanosized oxide powders by flame spray pyrolysis of novel alkoxide aluminate and silicate complexes as well as other soluble metal complexes. This scaleable synthesis route provides reproducible, high purity nanosized powders. We have previously studied single crystal TiO_2, CeO_2, crystalline

mullite ($3Al_2O_3cot2SiO_2$), and amorphous strontium aluminosilicate ($SrO \cdot Al_2O_3 \cdot 2SiO_2$) powders with particle sizes of 2-200 nm (ave. = 75 nm) and surface areas = 40-60 m2/g at production rates * 250 g/h. The powders are characterized using a variety of techniques. The poster will focus on the utility of the FSP method to provide control of multimetallic concentrations from line compounds down to to ppm level, the formation of selected matrices and the potential to optimize sintering, lasing and other desired properties.

K3.3
HIGH-TEMPERATURE OXIDATION RESISTANCE OF ZrO_2 COATINGS ON Ti-6A1-4V ALLOY BY ATMOSPHERIC PLASMA SPRAY. K. Park, Department of Materials Science and Engineering, Chung-ju National University, Chung-ju, KOREA; B. Il. Kang, K.-B. Kim, Department of Materials Engineering, Hankuk Aviation University, Koyang, KOREA.

ZrO_2 was deposited on Ni Cr-Al-Co-Y under coating (~50 μm) on Ti 6Al-4V substrate by atmospheric plasma spray at D.C. 65 V and 500 A under a mixed gas of 75% Ar and 25% II_2. The microstructure and morphology of the coating layers were examined by scanning electron microscopy. ZrO_2 (t ZrO_2 and m-ZrO_2) single coating layer (~100 μm) was formed on the under coating. To investigate the high-temperature oxidation resistance of the specimens, they were heated at both 700 and 800°C in air under atmospheric pressure The weight of the specimens was measured up to 200 hours. The specimens were cooled to room temperature in air before measuring the weight. After the weight measurements, the specimens were inserted within the furnace. After oxidation tests, the crystalline structure and chemistry of oxidized products formed on the Ti-6A1-4V substrate were investigated by X-ray difffraction, scanning electron microscopy, and electron probe microanalysis. TiO_2 and Al_2O_3 oxides were formed after oxidation tests. At 700°C oxidation tests, the weight of ZrO_2 coated Ti 6Al-4V alloy increased up to 50 hours owing to the formation of TiO_2 and Al_2O_3 oxides and then decreased owing to the spallation of the oxides, whereas at 800°C oxidation tests that of ZrO_2 coated Ti-6Al-4V alloy increased up to 100 hours and then decreased.

K3.4
PHASE COMPLEXITY OF HYDROXYAPATITE COATINGS OBTAINED BY PLASMA SPRAYING. C.F. Feng, K.A. Khor, W.K. Kweh School of Mechanical & Production Engineering Nanyang Technological University, SINGAPORE.

Hydroxyapatite (HA), an interesting bioactive material, is often applied clinically as a coating on an inert metallic implant. However, calcium phosphate phases other than crystalline HA are usually identified in the HA coatings obtained by plasma spraying (a widely used coating process). These phases include amorphous calcium phosphate, tricalcium phosphate (TCP), tetra-calcium phosphate (TTCP) and CaO. They do not possess bioactive properties. In this study we aim to understand the phase complexity of the HA coatings by gaining insights into the phase evolution of HA powders associated with the plasma spray process. The phase transformations during the heating process are investigated by DSC and XRD; those during the cooling are proposed in the light of the actual cooling conditions with the help of the phase diagram, which is verified by experimental evidences. The discussion qualitatively explains the availability of amorphous HA, TCP, TTCP and CaO in the coatings as well as the dependence of their relative amounts on the thermal conditions and particle sizes.

K3.5
ASYMPTOTIC THEORY OF MELT DROPLET SPREADING AT PLASMA SPRAYING. Ruslan Abdulkhalikov, Alexander Fedorchenko, Inst of Thermophysics SB RAS, Novosibirsk, RUSSIA.

The analysis of solidified splats at plasma spraying shows that solidification of the drops in the form of disks with constant height is the exception rather than the rule. But in spite of wide variety of splat forms some general characteristic properties can be highlighted. The loss of axis symmetry and formation of ring blob on the front boundary of solidified drop are typical for the most splat forms. It is obvious that splat form influences on such properties of coating as porosity, adhesive and cohesive properties and phase properties of structure elements of coating. Therefore theoretical works devoted to the modeling of coatings applying, based on the simplest form of solidified particles - the disks with constant height are far from reality. But up to now there are not only quantitative, but also qualitative theories explaining the fingers formation at drop impact on the surface and taking into account ring blob formation on the front boundary of spreading drop. Therefore we will try to consider all above mentioned problems in the paper.

K3.6
SPLASHING MECHANISM OF MOLTEN DROPLET IMPACTING ON SUBSTRATE: ROLE OF ADSORBATES ON SUBSTRATE. Xiangyang Jiang, Yuepeng Wan and Sanjay Sampath, State University of New York at Stony Brook, Center for Thermal Spray Research, Department of Material Science and Engineering, Stony Brook, NY.

Splashing of molten droplets is a commonly observed phenomena in many metallurgical processes which involves the impact of molten droplets on a substrate; splat cooling, thermal spray, spray forming and microcasting, etc. Fundamental understanding of splashing mechanism is of not only of academic curiosity, but bears technical significance. It was found as early as 1920's that substrate temperature has strong effect on splat morphology. With the increase of substrate temperature from room temperature, splat morphology changes gradually from highly splashing to contiguous. Based on several specific substrate/droplet systems being investigated, various hypotheses have been suggested, which attribute this phenomenon to the solidification process of the impacting droplet, substrate oxidation and wettability. However, none of these hypotheses can be used to explain the universal phenomena observed in different systems. One attribute that has received limited attention is the gases adsorption on the substrate surface. The presence of adsorbed gases on surfaces is universal for most solids; the gases releasing caused by the steep temperature rising due to the impinging thermal droplet may lead to splashing, and preheating the substrate eliminates this effect. Experiments were carried out to verify the hypothesis. Highly splashed zirconia splats were prepared with RF torch in low-pressure chamber on cold, polished steel substrate. In another run, substrate was put in the evacuated chamber and heated up to remove the adsorbed gases; then the substrate was cooled down in vacuum to ambient temperature before splats were prepared on it. Obtained splats were much more contiguous. This result reveals the important role of adsorbed gases on the splat morphology.

K3.7
SYNTHESIS OF THERMAL SPRAY COATING MATERIALS VIA THE SHS. Dae-Kyu Chang, Chang-Yul Suh, Materials Development Division, Korea Institute of Geology, Mining and Materials, Taejon, KOREA.

Molybdenum based thermal spray coatings are commonly used in the production of piston rings and synchronizer for internal combustion engines, due to their excellent scuff resistance. MoSi2 materials for using thermal spray coating were synthesized via SHS. SHS(Self-propagating High temperature Synthesis) has been developed over last 10 years and is a combustion synthesis process via which basic elemental constituents are mixed and then reacted. we observe that the powder-mixed Mo-Si-Al shows maximum reactivity, which arises from the efficient mixing of the Al and Si powders. The reaction to form Mo(SiAl)2 composities occurs at about 915°, this was confirmed by DTA and thermocouple. In a making an actual sample, this reaction at 656° is sufficiently endothermic reaction to ignite the reaction at 915°. A rapid rise in the temperature between room temperature and about 1380° take place about 24sec. The aluminum-silicon eutectic liquid phase first forms at a temperature below the initiation point of the combustion reaction. This transient liquid phase then spreads via capillarity around the reactant particles, which leads to densification and synthesis process. The porous solid has a sponge-like appearance that closely resembles that of a typical porous SHS product. Moreover, the surface is extensively marked by small and large holes. These holes can be attributed to the outgassing of absorbed gases on powder particles. The final product density increased as the cold-compacting pressure(green sample density) increased. Major diffraction peaks are attribution to a C40-type phase, i.e., Mo(SiAl)2 in the present study; some minor peaks have been identified as the Al3.21Si0.47 phases.

K3.8
SYNTHESIS AND CHARACTERIZATION OF LITHIUM TITANATE POWDER BY ULTRASONIC MIST COMBUSTION PROCESS. C.H. Jung, J.Y. Park, J.I. Kim, G.W. Hong, Korea Atomic Energy Research Institute, Functional Materials Dev, Taejon, KOREA; D.K. Kim and C.H. Kim, Korea Advanced Institute of Science and Technology, Dept of Materials Sci & Eng, Taejon, KOREA.

Lithium-based ceramics have been recognized as promising tritium-breeding materials for fusion reactor blankets. Recently Li_2TiO_3, a low activation ceramics, were selected as the breeder material due to its excellent tritium release behavior at low temperature. The ultrasonic-mist-combustion process (UMCP), which is the self-sustaining oxidation-reduction reaction between metal nitrates and organic fuel with ultrasonically induced spherical mist, is applied to the formation of tritium breeding ceramic powders. While the shape of the powder could not control by a general combustion process, the synthesized powder by UMCP consisted of the micrometer-sized spherical particles with nano-sized primary particles. Using this powder, the enhanced sinterability of Li_2TiO_3 can be

obtained. By XRD, SEM, TEM, DTA/TG and dilatometer, characterization and the sintering behaviors of ultrasonic-mist-combustion synthesized powder will be discussed.

SESSION K4: SYNTHESIS OF POWDERS AND NANOSTRUCTURED MATERIALS

Chairs: Christopher C. Berndt and Joachim Heberlein
Tuesday Morning, November 30, 1999
Room 308 (H)

8:30 AM *K4.1
CERAMIC POWDER SYNTHESIS IN NON-TRANSFERRED ARC THERMAL PLASMA REACTORS. Patrick R. Taylor, Plasma Processing Laboratory, Department of Metallurgical & Mining Engineering, University of Idaho, Moscow, ID.

New reactors to perform ceramic powder synthesis using thermal plasma technology requires the development of new experimental techniques and analysis. Among the advantages of thermal plasma processing are the following: (1) very high temperatures and concentrated enthalpy, (2) clean and adjustable (oxidizing, reducing or inert) reaction environments, and (3) high throughput in small reactors (enhanced heat and mass transfer rates and chemical kinetics). This paper discusses several reactors and chemical reactions developed to take advantage of these qualities. The high temperatures available in these reactors allows for the vaporization of almost any feed material and the steep temperature gradients available allow for the formation of both metastable phase and very fine product particle sizes by rapid quenching. This has led to the investigation of the formation of a variety of ultra fine ceramic powders. The experiments are typically performed using instrumentation that allows for both the steady state operation of the reactor and the development of overall energy and materials balances. The results of the experiments are determined by the utilization of a variety of analytical techniques on the products that are formed. It is very difficult to obtain direct measurements of the reactions,as they are occur, due to the very high temperatures in the reactor and the very small particle size of the products. Examples are given for several chemical synthesis systems, including: barium strontium titanate, barium ferrite, boron nitride and iron-titanium carbide.

9:00 AM *K4.2
INDUCTION PLASMA SYNTHESIS AND PROCESSING OF MATERIALS. Maher I. Boulos, Plasma Technology Research Centre (CRTP), Université de Sherbrooke, Dept. of Chemical Engineering, Faculty of Engineer, Sherbrooke, Québec, CANADA.

An increasing attention has been given over the past decade to the potential use of induction plasma technology for the synthesis and processing of high added value materials. The synthesis of ultrafine powder of metals and ceramics is a typical example where pure and composite powders could be prepared through the in-flight vaporization of the precursor elements followed by the condensation of the vapor clouds under controlled conditions. The plasma spraying of metals and ceramics is another example of in-flight processing of the feed material in powder form followed by its rapid solidification on the substrate in the form of a coating or near net shape part. The process can involve a physical and/or a chemical transformation of the material in the case of reactive deposition techniques. A review will be presented of highlights of technology and science base developments in this area giving typical examples of ultrafine powder production and induction plasma spraying applications. Research needs are to be outlined together with potential developments in this area.

9:30 AM *K4.3
FABRICATION OF CARBON POWDERS WITH UNIQUE MICRO-STRUCTURE BY RF INDUCTION PLASMA SPRAYING. Takamasa Ishigaki, National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki, JAPAN.

The present work concerns on a novel application of the materials synthesis by thermal plasma spraying. Carbonaceous materials as an anode of lithium secondary batteries, which have the highest theoretical energy density, have been studied extensively. Recently, it has been reported that some kinds of disordered carbonaceous materials have a higher capacity than 372 mAh/g of the theoretical capacity of graphite. The disordered carbonaceous materials derived from polymer precursors contain some functional groups, such as =CO, -OH and -COOH. The residual functional groups and/or hereto atoms, such as hydrogen, nitrogen and oxygen, have been believed to have an influence on the anode characteristics. In this work, porous carbon powders were directly prepared from phenolic resin powders by the RF induction thermal plasma spraying and applied to the anode materials of lithium secondary batteries. Spherical phenolic resin powder of 16 and 27 micro-meters in average particle size was axially injected into the center of the Ar-H2 and Ar-N2 RF induction thermal plasmas with Ar carrier gas, with the intention to control the plasma heating and chemical reactions. The plasma heating induced the decomposition of phenolic resin and the partial evaporation. In order to suppress the formation of ultra fine particles coagulated from a vapor phase, CO2 was added to the powder carrier gas both in the Ar-H2 and Ar-N2 plasma treatment. The chemical composition of the plasma-prepared powders strongly depended on the plasma conditions. The powders remained spherical, however, they became very porous and showed the unique microstructure. Micro-Raman scattering spectroscopy and TEM observation suggested the non-uniform distribution of highly graphitized and amorphous areas in the radial direction of powder particles. In the electrochemical measurements as an anode of lithium secondary battery, the plasma-prepared powders exhibited the better charge/discharge characteristic than the carbon powders derived from phenolic resin by conventional heating.

10:30 AM *K4.4
HYPERSONIC PLASMA PARTICLE DEPOSITION OF LARGE-AREA AND PATTERNED NANOSTRUCTURED FILMS. D.I. Iordanoglou, F. Di Fonzo, M.H. Fan, A. Gidwani, D. Neumann, P.H. McMurry, J.V.R. Heberlein, S.L. Girshick, Univ of Minnesota, Dept of Mechanical Engineering, Minneapolis, MN; N. Tymiak, W.W. Gerberich, Univ of Minnesota, Dept of Chemical Engineering, Minneapolis, MN; N.P. Rao, MicroTherm, LLC, Minneapolis, MN.

We have developed a new method for depositing nanostructured coatings, known as hypersonic plasma particle deposition. In this method gaseous reactants are injected into a thermal plasma, which is then expanded through a nozzle, with the pressure dropping from slightly subatmospheric to about 2 Torr. The resulting sharp temperature drop in the nozzle drives the nucleation of nanoparticles, which issue into the low-pressure expansion and are accelerated by the highly supersonic flow. These particles are then deposited by either of two processes: large-area deposition or focused deposition for patterned films. In large-area deposition the substrate to be coated is placed shortly downstream of the nozzle exit, and particles in the expanded jet deposit on the substrate by inertial impaction. In focused deposition the substrate is replaced by a series of aerodynamic lenses, which focus all particles within a defined size range into a narrow collimated beam. These particles then deposit by inertial impaction on a translatable substrate which is located in a second chamber, at a pressure around 0.7 Pa (5 mTorr). We have deposited nanostructured silicon carbide films with both processes. Silicon tetrachloride and methane are injected into an argon-hydrogen plasma which is generated by a DC torch. The particles produced in the nozzle expansion have a narrow size distribution, with a mean diameter typically around 20 nm. In the large-area deposition experiments the 2-cm-diameter molybdenum substrate is completely coated, with linear deposition rates typically around 150 microns/hr. The deposits clearly show grains in the 20-30 nm size range, with as-deposited densities as high as 90% of theoretical SiC. In the focused deposition experiments we have written lines by translating the substrate. A line width around 100 microns was achieved for monodisperse 17-nm particles with a linear deposition rate of 1.5 microns/sec.

11:00 AM K4.5
SYNTHESIS OF NANOSTRUCTURED Si-B-C-N COATINGS BY REACTIVE SUSPENSION PLASMA SPRAYING. Etienne Bouyer, Matthias Müller, Gunther Schiller, Rudolph Henne, German Aerospace Center, Inst of Technical Thermodynamics, Stuttgart, GERMANY.

During the last decade the field of nanostructured materials became of great interest, because of the specific and unique properties of such type of materials. The enhanced properties include strength/hardness, ductility/toughness, reduced density, reduced elastic modulus, higher electrical resistivity, increased specific heat, higher thermal expansion coefficient and lower thermal conductivity. A rather wide range of experimental techniques have already been developed up to now for the processing of nanomaterials. Due to the high quenching rate (10^5 to 10^8 K/s), the thermal plasma technology is an appropriate and successful technique which permits to synthesize nanostructured materials (powders as well as deposits). DC plasma spraying of liquid precursor enables to synthesize with success ceramic oxide, nevertheless, post-spray treatment is needed to produce dense oxide deposits with nanosized grains. In this paper a process based on both the Thermal Plasma Chemical Vapor Deposition (TPCVD) and the Suspension Plasma Spraying (SPS) applied on RF induction plasma for ceramic coating preparation is presented. The starting materials are liquid aminosilane or chlorosilane type compounds which are by-products coming from the silicon industry (Mller-Rochow process) with submicronic B_4C powders suspended in it. Si-B-C-N coatings on Mo substrate with a deposition rate up to 10μm/min are synthesized by this way. Such a deposition rate is two to three orders of magnitude faster compared to conventional CVD/PVD techniques. The phases composition of the resulting coatings are investigated by

means of SEM and XRD. Results on the influence of the processing parameters (i.e. pressure, spray distance, plasma gas nature and composition) on the coating phase and microstructure is presented. RF plasma synthesis and deposition coupled with the use of cost-effective silane precursors -as they are available from the silicon industry- is a competitive economical process for the production of high-performance Si-based ceramic coatings.

11:15 AM K4.6
NANOPOWDER-BASED FEEDSTOCK POWDERS FOR THERMAL SPRAYED COATINGS. Ganesh Skandan, Nanopowder Enterprises Inc., Piscataway, NJ; Rajendra Sadangi, Bernard H. Kear, Rutgers-The State University of New Jersey, Piscataway, NJ; Lucy Liu, YunFei Qiao, and Traugott Fischer, Stevens Institute of Technology, Hoboken, NJ.

During the past few years, there has been a great deal of interest in forming nanostructured thermal sprayed coatings, particularly in the area of hardmetals such as WC/Co. This interest stems from the fact that unique properties that have been achieved in bulk materials synthesized from nanostructured WC/Co powders. However, progress in forming nanocrystalline coatings by Plasma and HVOF thermal spraying has been hampered by difficulty in feeding nanoparticles through the spray gun, combined with the problem of decarburization of the WC phase into W2C and other W-rich phases. The resulting coating has reduced toughness and ductility, and displays poor abrasive and sliding wear resistance. We have developed a feedstock material that is a blend of nanocrystalline and conventional coarse grained thermal spray grade powders. The HVOF sprayed coating, which has a bimodal grain size distribution, has high hardness and superior abrasion wear resistance (wear rate ~ 0.3 x 10-6 mm3/Nm) than coatings produced using other powders. There was virtually no decarburization and thick coatings were easily formed. The correlation between feedstock material and coatings characteristics will be described.

11:30 AM K4.7
ABILITY AND MECHANISMS OF AMORPHOUS AND NANOCRYSTALLINE PHASE SYNTHESIS BY THERMAL SPRAYING. Tetyana Shmyreva, TAFA Inc., Concord, NH.

X-ray diffraction precision technique, transmission and scanning electron microscopy, differential scanning microcalorimetry, potentiodynamic electrochemical measurement of corrosion property, measurement of hardness and heart treatment were carried out for Detonation, Plasma and HVOF coatings from eutectic iron and nickel base alloys and from tungsten carbide plus metal compositions. Phase transformation mechanisms and ways to form nanostructured, amorphous and composite structure and to imrove coating properties are discussed.

11:45 AM K4.8
THE EFFECT OF WC SIZE ON STRUCTURE-WEAR RELATIONSHIPS IN HVOF SPRAYED WC-Co COATINGS. Andrew H. Dent, Steve DePalo, Sanjay Sampath, Herbert Herman, Center for Thermal Spray Research, SUNY, Stony Brook, NY.

With the increased interest in recent years regarding the properties of thermally sprayed WC-Co cermets with nanograin carbide particles, it is important that the effect of carbide size with respect to both decomposition of the material during deposition and the resultant wear properties of the coating be fully understood. To this end, a systematic study of a range of thermally sprayed WC-18Co powders with different average WC sizes from up to 10μm to sub-micron level has been undertaken. These materials have all been deposited using the JetKote HVOF system. Examination of the primary coating layer in the form of single splats as well as the fully consolidated coatings has been conducted using general area and microfocus X-Ray diffraction (XRD), high resolution scanning electron microscopy (SEM) and cross-sectional transmission electron microscopy (TEM). Wear analysis and fracture toughness measurements have shown a strong property dependance on carbide size. Detailed microstructural and phase analysis of single splat deposits will be presented and related to both processing parameters and the wear properties of this series of WC-Co cermets.

SESSION K5: NEW PROCESSES FOR POWDER AND COATING FORMATION AND EVALUATION

Chairs: Y. C. Lau and Sanjay Sampath
Tuesday Afternoon, November 30, 1999
Room 308 (H)

1:30 PM *K5.1
A METHOD FOR PRODUCTION OF METAL VAPOUR UNDER PLASMA CONDITIONS. Jawad Haidar, CSIRO Telecommunications and Industrial Physics, Sydney, AUSTRALIA.

For processes such as film deposition and powder synthesis, the presence of metal vapour under plasma conditions helps improve the yield of the process, often resulting in a higher efficiency and improved end results. For deposition of films, the presence of metal vapour ions helps increase film adhesion to the substrate and improve bonding, resulting in higher film qualities. For films of composite materials and also for synthesis of powders such as oxides and nitrides, the presence of atomic and ionised species increases the reaction rates between the precursor metal vapour and the reacting gases. In this paper we present a new technique for production of metal vapour under plasma conditions for use in film deposition, coating and powder synthesis. The technique allows for generation of high evaporation rates from solid precursor metals at pressures ranging from vacuum up to several atmospheres. The technique has been used for production of nano-size metal and oxide powders of aluminium and nickel. For film deposition at a low pressure we have obtained deposition rates exceeding most existing techniques for films of aluminium and nickel. Details about the technique together with examples of applications in both film deposition and powder production will be presented at the meeting.

2:00 PM *K5.2
COLD SPRAY – HIGH RATE DEPOSITION OF THICK METAL COATINGS WITHOUT MELTING. Mark F. Smith, Richard A. Neiser, Delwyn L. Gilmore, Ronald C. Dykhuizen, and John E. Brockmann, Sandia National Laboratories, Albuquerque, NM.

Cold Spray is an emerging technology from the Former Soviet Union that has been used to deposit a wide range of pure metals, metal alloys, and even some composite materials at or near room temperature. In this process, solid (unmelted) powder particles are accelerated up to high velocities (typically greater than 500 m/s) in a supersonic jet of compressed gas and impact the target surface with sufficient energy to forge-weld themselves to the surface. Cold spray offers the possibility of rapidly consolidating metal powders to build up coatings or free-standing shapes without melting, solidification, pressing, or sintering. Because the impacting particles are not significantly heated, metals have been deposited in an ambient-air environment without measurable increases in oxygen as compared to the feedstock powder. Unlike thermal spray deposition, residual stress in cold-sprayed materials is typically compressive rather than tensile, so very thick deposits can be achieved without cracking. Deposition efficiencies greater than 98% and as-deposited densities of 99.6% of theoretical density have been achieved. Copper cold-spray deposited in an ambient-air environment was found to have a thermal conductivity more than 80% of that for Oxygen-Free High-Conductivity (OFHC) copper. The spray plume is very sharply defined, so little or no masking is needed. In addition, some materials do not require any surface preparation, such as grit blasting, prior to coating deposition. The ability to consolidate materials in this manner also offers interesting new possibilities in areas such as nanophase materials and direct fabrication from computer models. A discussion of this intriguing new technology and ongoing research at Sandia National Laboratories will be presented.

2:30 PM K5.3
USE OF LIQUID ORGANOMETALLIC PRECURSOR MATERIALS IN THE COLD GAS DYNAMIC SPRAY PROCESS. Vijay Shukla, Greg Elliott, Bernard Kear, Rutgers University, New Brunswick, NJ.

With a view towards developing the next generation of coatings, cold gas dynamic spray (CGDS) technique is being improved. In this method the material to be coated, is injected into a supersonic rectangular jet (design Mach number of 3.2, with rectangular exit of 3.17 mm × 16.76 mm) which impinges on the surface to be coated. In this process normally material in powder form is used. A powder feeder, designed for use with nanopowder agglomerates, is used to inject powders near the nozzle throat. The powder gains speed through momentum transfer from the jet and bonds on the substrate (surface to be coated) due to the kinetic energy of the nanopowder. Several coatings using 3-5 micron size copper and nanopowder *WC* on steel and aluminum substrates have been produced. The benefit of this process is that the material does not undergo any chemical changes during formation of coatings. The flapping modes produced by supersonic jet impingement are studied to improve the coatings produced. The powder particle velocities have been measured using particle image velocimetry. As part of this study an improvement to the CGDS system has been developed to enable use of liquid metal precursors in this coating process. A high pressure liquid feeder designed for use with liquid precursors has been used along with a preheater to form powder as part of the CGDS process. Preliminary results of forming silicon coatings using this modified CGDS will be presented.

3:15 PM K5.4
PULSED MAGNETIC FIELD ASSISTED THERMAL SPRAYING SYNTHESIS OF SULFIDES AND OXIDES OF METALS FILMS.

Mark N. Levin, Voronezh State Univ, Nuclear Phys. Dept, Voronezh, RUSSIA; Victor N. Semenov, Voronezh State Univ, Inorganic Chem. Dept, Voronezh, RUSSIA.

We reported earlier [1] that pulsed magnetic field (PMF) treatment of mono-crystalline silicon suppresses hydrophobity of it's surface and allows one to perform synthesis of thin films on the silicon substrates by thermal spraying of the relevant aqueous solutions. Now we present results of synthesis of sulfides and oxides of metals on silicon and glass substrates by thermal spraying with the following PMF processing of the deposited films. The proposed two stages process makes it possible to control composition of the synthesizing films at the first stage of the process and to control microstructure of the films at the second one. Luminescent layers of CdS, ZnS and $Cd_xZn_{1-x}S$ doped with Cu, Ag and/or Mn activators were deposited by spraying of aqueous solutions of thiocarbomide complexes of metals $Me(N_2H_4CS)_2Cl_2$ doped with copper, silver and/or manganese salts. The PMF processing of the synthesized films essentially enhanced intensity of luminescence and allows one to control decay and recovery times of the luminescence. Multi-layered structures SnO_2-$Cd_xZn_{1-x}S$-Cu_2S were synthesized by thermal spraying for fotovoltaic applications. The transparent and highly conductive SnO_2 films were synthesized by spraying of doped aqueous solutions of $SnCl_4$. The PMF processing of the synthesized structures tends to increase the idling voltage of the fotovoltaic effect.

1. M. Levin, V. Semenov, MRS Spring Meet. Abstr., J13.13, 1996

3:30 PM K5.5
Abstract Withdrawn.

3:45 PM K5.6
LASER ASSISTED PLASMA SPRAY METHOD FOR SYNTHESIS OF TRIBO-MATERIALS. Shinya Sasaki, Shazad Alam, Hirofumi Shimura, Seisuke Kano, Mechanical Engineering Laboratory, Tsukuba, JAPAN; Yuji Kawakami, Vaccum Metallurgical Co., Ltd, Chiba, JAPAN.

Structural materials for machine elements are required to have two characteristics; one concerns the bulk structure and the other is related to the surface, but these properties are often inconsistent. Surface modification is a valuable technique that makes it possible to add new properties on the surface, unrelated to the internal bulk properties. It is commonly accomplished by coating. The coating films for the tribo-elements must be thick enough to have a long lifetime against the sliding wear. Advantages of plasma spraying include: very high deposition rate; a large area can easily be coated with thick film; and there are few limitations on the coating materials. However, the plasma spray film has the disadvantages of high porosity and low adhesiveness. These disadvantages restrict the application of plasma spray coatings to tribo-elements. In order to improve qualities of the plasma spray films, we developed a laser assisted plasma spraying system , which consists of a high power CO_2 laser with a low pressure plasma spraying system. In order to clarify simultaneous laser beam irradiation effects on tribological properties, we synthesized several metal and ceramic films. The tribological properties of the coated films were evaluated by a sliding tester and a scratch tester. Results of experiments showed that it should be possible to produce a high performance tribo-material possessing better adhesiveness and little micro-porosity. Analytical results by XRD suggest that meta-stable state were formed by laser irradiation during the spraying process, which is considered to be closely related to anti-wear and low friction mechanism of laser assisted plasma spray films.

4:00 PM K5.7
ANALYSIS OF CRACKING IN THERMALLY SPRAYED CERAMIC SPLATS. Srini Rangarajan, Alexander H. King, Dept. of Materials Science & Engineering, SUNY, Stony Brook, NY.

Plasma sprayed yttria-stabilized zirconia obtained as splats on stainless steel substrates constitute the building blocks of thick coatings. The splats exhibit extensive cracking due to the tensile stresses generated during rapid solidification and cooling of plasma melted ceramic particles on stainless steel substrate. This is believed to be a result of the constraint to contraction during cooling from the melting point of the sprayed material to the substrate temperature. The constraint is provided by the adhesion of the ceramic splat to the metal substrate. The extent of tensile stress and cracking is a function of the strength of interfacial adhesion. This is the premise of this investigation to determine the interfacial adhesion strength at the ceramic-metal interface. Detailed study of the nature of cracking in terms of crack density, orientation and distribution over the splat has been carried out from SEM images of individual splats of varying sizes obtained on substrates at different temperatures. Splats on cold substrates show very little adhesion and sparse cracking while those obtained on hotter substrates show better adhesion and denser crack networks. Cracks are predominantly radial and exclusively so in the splat periphery. Central portions show dense cracking. There is gradual decrease in crack densities with increasing splat sizes. This analysis of cracking is expected to reveal details of the stresses over the area of a single splat unlike direct techniques of measurement. Acknowledgement: This work is supported by the National Science Foundation, MRSEC program, Grant No. DMR 9632570.

4:15 PM K5.8
INTERNAL SURFACE AREA DISTRIBUTIONS IN THIN THERMAL SPRAY COATINGS STUDIED BY NEAR-SURFACE SMALL-ANGLE NEUTRON SCATTERING. H. Boukari[1,2], A.J. Allen[1], G.G. Long[1] and J. Ilavsky[1,2]. [1]MSEL, NIST, Gaithersburg, Maryland,[2]University of Maryland, College Park, MD.

We have applied near-surface small-angle neutron scattering (NS-SANS) technique to determine the surface-areas of thin (150-250 micron) yttrium stabilized zirconia (YSZ) coatings deposited on a substrate. In these experiments, a near-horizon, glancing incident beam is directed at the 25×25 mm^2 surface of the sample, and the resulting refracted beam is used as the main beam for scattering inside the coating. The technique enables the microstructural characterization of the surfaces of these samples, which cannot be easily measured by conventional SANS in transmission mode. We describe the details of the method,its advantages such as control of the penetration depth by varying the incidence angle and improved signal-to-noise, and its limitations. Further, we report surface-area measurements of plasma-sprayed YSZ coatings which are known to contain intra-splat cracks, inter-splat pores, and globular pores. We discuss the results and compare them with those obtained from conventional SANS experiments performed on similar thick (4-5 mm) deposits.

4:30 PM K5.9
PHASE STRUCTURE OF QUASICRYSTALLINE COATINGS PREPARED BY THERMAL SPRAYING. C.I. Lang,University of Cape Town, Dept of Materials Engineering, Cape Town, SOUTH AFRICA; A. Duckham, National Institute of Standards and Technology, Materials Science and Engineering Laboratory, Gaithersburg, Md; F.S. Biancaniello, National Institute of Standards and Technology, Metallurgy Division, Gaithersburg, Md; D. Shechtman, Technion - Israel Institute of Technology, Dept of Materials Engineering, ISRAEL.

Quasicrystalline (QC) materials exhibit many useful properties as a result of their unique structure, including desirable surface properties such as high hardness and low friction coefficient. However, their very low fracture toughness precludes their utilisation in bulk form. As a consequence, the preparation of QC materials in coating form has received considerable attention as a method of exploiting their good surface properties together with the toughness of metallic substrates. The phase structure of QC powders used in the thermal spray process is however not necessarily retained in the resulting coating. We have investigated thermally-sprayed coatings of several QC materials, including QC materials which contain icosahedral phases, decagonal phases or both. Comparison of the phase structures of the QC starting powders and the sprayed coatings shows that the appearance of a second or third phase is common as a result of thermal spraying. After thermal spraying we have observed the appearance, in different alloy systems, of crystalline phases and of quasicrystalline phases different to those observed in the starting powder. Heat treatment after thermal spraying may further alter the phases present and their relative volume fraction. These observations are considered in relation to the powder atomisation and thermal spray processes.